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have the tautomeric structures, RC(OMe) (:NHal) or RCO.N(Me)Hal . This complication does not exist in the case of triphenylmethyl halogen amines $(\text{C}_6\text{H}_5)_3\text{C.NHHal}$, whose metal derivatives could only have the definite structure $(\text{C}_6\text{H}_5)_3\text{C.N(Me)Hal}$. A successful molecular rearrangement of these halogen amines by bases would give convincing evidence as to the nature of the salt formed in initiating the rearrangement and would give strong presumptive evidence in favor of the view that in the rearrangement of acyl halogen amines, the salts RCO.NMeHal are the ones directly concerned in the rearrangement.

Further: chloroimidoketones $(\text{C}_6\text{H}_5)_2\text{C:N}^+\text{Cl}$ have been found to resist rearrangement¹⁹ in spite of the presence of the unstable positive chlorine atom (see part I). This result was not unexpected from the point of view of the theory of the one of us concerning the mechanism of these molecular rearrangements:⁴ the theory postulates that the easiest path to a rearrangement is through the intermediate formation of univalent nitrogen derivatives $\text{RCO.N} <$, $\text{R}_3\text{C.N} <$ (see equation 3), the free valences of the univalent nitrogen being considered sufficiently powerful to tear the radicle R from the carbon and thus effect the rearrangement to a more stable molecule (see equation 3). The significance of the intermediate formation of a univalent nitrogen derivative in relation to the electron theory is discussed later on in the text. Triphenylmethyl halogen amines, $\text{R}_3\text{C.NH(Hal)}$ and $\text{R}_3\text{C.N(Hal)}_2$, in contrast with the chloroimidoketones $\text{R}_2\text{C:NCl}$, present the opportunity for an unhampered formation of the univalent nitrogen derivative $\text{R}_3\text{C.N} <$ by the loss of H(Hal) or $(\text{Hal})_2$ under suitable experimental conditions. They were therefore expected to be easily subject to rearrangement.

This investigation was undertaken with the object of deciding the questions indicated and thus throwing light on the whole problem of these molecular rearrangements. The experimental results confirmed in every respect the theoretical anticipations. Of the facts established and their bearing, the following are the most important:

1. A number of triphenylmethyl halogen amines— $(\text{C}_6\text{H}_5)_3\text{C.NHBr}$, $(\text{ClC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{C.NHCl}$, $(\text{BrC}_6\text{H}_4)(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C.NHCl}$, and $(\text{C}_6\text{H}_5)_3\text{C.NCl}_2$ and $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NCl}_2$ —were found to undergo under suitable conditions a molecular rearrangement into phenylimido benzophenones $\text{R}_2\text{C:NR}$ (see equation 3). The rearrangement was established in the case of the first compound listed by the identification of the phenylimido benzophenone $(\text{C}_6\text{H}_5)_2\text{C:NC}_6\text{H}_5$ (yellow crystals, m.p. 110° ; the melting-point of a mixture of the product with synthetic substance (m.p. 111° – 112°) was found at 111°) and by the identification of the benzophenone (m.p. 47°) and aniline (bleaching-powder test; the

chloroplatinate gave 32.41% platinum, theory 32.74%) produced by the hydrolysis of the imido ketone (see equation 4). In the rearrangement of the chloroamines containing substituted phenyl groups, mixtures result: in a fraction of the rearranging molecules the substituted phenyl radicle migrates to the nitrogen, in the remainder the phenyl group itself leaves the carbon for the nitrogen. Thus, in the rearrangement of di-parachlorophenyl-phenyl methylchloroamine (the second compound listed above), the two substances $(\text{C}_6\text{H}_4\text{Cl})_2\text{C}:\text{NC}_6\text{H}_5$ and $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C}:\text{NC}_6\text{H}_4\text{Cl}$ are formed. This was established by the separation and identification of their respective products of hydrolysis (equation 4), dichlorobenzophenone $(\text{ClC}_6\text{H}_4)_2\text{CO}$ (m.p. 141°) and aniline (bleaching-powder test), and chlorobenzophenone $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CO}$ (m.p. 77°) and chloroaniline (m.p. 70°). In each instance the melting-point of a mixture of the substance obtained with the corresponding synthetic product was taken to complete the identification. The ratios in which the various radicles migrate to the nitrogen in the rearrangements was determined by quantitative examinations of the anilines formed: for the instance just discussed, the ratio of chloroaniline to aniline was found to be 68/32, in molar terms—in other words, the two radicles share in the migration very closely in the same ratio as they are found in the original molecule.

2. The reagents used to effect the rearrangements are those which the univalent nitrogen theory would postulate: bases (sodium and calcium hydroxides, sodium methylate) were used for the rearrangement of the monohalogenamines to facilitate the loss of halogen acid; and, characteristically, heat alone was sufficient to cause the loss of chlorine with explosive violence by the dichloroamines, the rearrangement ensuing:



3. A compound, triphenylmethylchloromethylamine $(\text{C}_6\text{H}_5)_3\text{C}.\text{N}(\text{CH}_3)\text{Cl}^+$, analogous to these rearranging bodies, with the exception that the well known stability of the union between nitrogen and the methyl radicle would interfere with the formation of a univalent nitrogen derivative, was found *not to be rearranged*, either by treatment with bases or by heat. A rearrangement would have produced a derivative of methylaniline (see below), which by hydrolysis would have given methylaniline. All the tests for methylaniline, even the exceedingly sensitive chloride of lime color test, showed its absence in the products of hydrolysis of the compounds formed under the conditions mentioned.

This important result shows that the tendency of a positive halogen

atom to go over into its stable negative form is not alone sufficient, as a rule, to cause the characteristic rearrangement of these compounds, but that the path to the formation of a univalent nitrogen derivative must usually, if not always, be open, this derivative being the substance that suffers the actual molecular rearrangement (see equation 3). This must signify that a positive halogen atom can secure two electrons from the nitrogen atom to which it is directly linked much more readily than from the carbon atom holding the nitrogen (see equation 3). Otherwise the rearrangement would proceed by a direct exchange of radicles following a migration of the electrons from the carbon to the halogen atom. Furthermore, the characteristic contrast shown in the behavior of the rearranging compounds ($R_3C.NH(Hal^+)$ —losing halogen acid—and $R_3C.NCl_2^+$ —losing chlorine—), on the one hand, and the non-rearranging compounds ($R_3C.N(CH_3)Cl^+$ and $R_2C:NCl^+$), on the other hand, leads to the important conclusion that the electrons most easily captured from the nitrogen atom by the positive halogen atom are *the two valence electrons* beyond the normal electrons of the nitrogen atom rather than any of the electrons of the normal atom. Otherwise, again, we should have a rearrangement by a direct exchange of radicles following the exchanges of electrons. This conclusion is included in equation 3 of the preceding paper.

The conclusions reached—(1) that a positive halogen atom can secure electrons more readily from the atom to which it is directly attached (nitrogen, in this case) than from one further removed from it, and (2) that the more readily available electrons are the two extra valence electrons of the nitrogen atom rather than its normal ones, seem not unreasonable. The second conclusion is in agreement with the observations of physical chemistry on the oxidation of negative ions like S^- , I^- , etc. This result seems to us the most important one established by the investigation, giving us a logical explanation, from the point of view of the electron theory of valence, of the real significance of the univalent nitrogen in the author's theory of the mechanism of this and similar rearrangements.

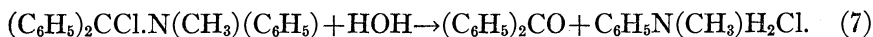
THE MOLECULAR REARRANGEMENT OF β -TRIPHENYLMETHYL
 β -METHYL HYDROXYLAMINE

WITH BERT ALLEN STAGNER

While a great mass of evidence, gathered by the author as well as independent investigators,⁴ has shown that the molecular rearrangements of halogen amines, hydroxylamine derivatives and azides seem to proceed preferably by the path of an intermediate formation of uni-

valent nitrogen derivatives, the theoretical possibility that another path might be taken toward the formation of more stable molecules has always been kept in mind. As a consequence, in the investigation of every new type of rearrangement, experiments have been included to attempt the rearrangement of compounds which could not readily form univalent nitrogen derivatives (see an instance above under 3). From this point of view, an attempt was made by the one of us and P. N. Leech to rearrange β -triphenylmethyl- β -methyl hydroxylamine $(\text{C}_6\text{H}_5)_3\text{C.N}(\text{CH}_3)\text{OH}$ by the same methods that had proved successful with triphenylmethylhydroxylamine $(\text{C}_6\text{H}_5)_3\text{C.NHOH}$. Indications of a rearrangement and the formation of a methylaniline derivative were indeed obtained,¹² but the evidence was quite uncertain, being limited to a general color reaction for monoalkylanilines and to some melting-point determinations of an acetyl derivative of the aniline.

We have now succeeded in establishing the fact that β -triphenylmethyl- β -methyl hydroxylamine is rearranged in a perfectly normal fashion by the action of phosphorus pentachloride on the ether solution of the hydroxylamine. The compound formed in the reaction was shown to be $(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5)$ [or its chloride $(\text{C}_6\text{H}_5)_2\text{CCl.N}(\text{CH}_3)(\text{C}_6\text{H}_5)$] by the identification of its products of hydrolysis, methylaniline and benzophenone:

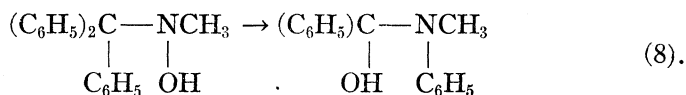


The formation of the more important component methylaniline was proved (1) by the analysis of its chloroplatinate (found, 31.40% platinum; theory 31.27%); (2) by the comparison of its hydrochloride with the hydrochloride of a known preparation of methylaniline (its melting-point was 119°–122°, that of the pure hydrochloride the same, and the melting-point of a mixture of the two salts the same); (3) by the navy blue color produced by the action of bleaching powder solution on the methylaniline. To these tests may be added the melting-point observations made with Leech on the acetyl derivative of the base. The benzophenone formed was also isolated and identified by its melting-point (47°).

It was further shown that chlorophenyl-diphenylmethyl- β -methyl hydroxylamine $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CN}(\text{CH}_3)\text{OH}$, like the corresponding chlorophenyl-diphenylmethylhydroxylamine $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NHOH}$, shows a migration of the phenyl group in a fraction of the rearranging molecules, a migration of the chlorophenyl radicle in the remainder. The molar ratio of methylaniline to chloromethylaniline was 75/25.

It is, therefore, now for the first time an established fact that sub-

stances which could not form simple univalent nitrogen derivatives may be rearranged in the same fashion as those which would easily lead to such derivatives and the theory of the rearrangements must now count with this fact. Whether we actually have a direct exchange of radicles

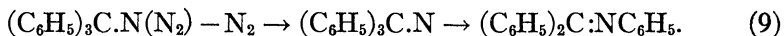


as postulated by Beckmann²⁰ for the analogous rearrangement of oximes $(\text{C}_6\text{H}_5)_2\text{C}:\text{NOH}$, or whether in both of these cases the rearrangements go by way of *salts* of univalent nitrogen derivatives, will be considered in detail in another place. It must suffice to point out here that whichever path the rearrangement follows, the final result is that the positive hydroxyl group of the hydroxylamines and of the oximes undoubtedly becomes a negative group in the course of the reaction: it still would be the unstable radicle in the original molecule and the satisfaction of its tendency to become negative would still be the prevailing influence in the rearrangement (see part I).

THE REARRANGEMENT OF TRIPHENYLMETHYL AZIDES AND OF SYM. DI-TRIPHENYLMETHYLHYDRAZINE

WITH JAMES KUHN SENIOR

While there may be some question as to the mechanism of the rearrangement of hydroxylamine derivatives (see above), the theory of a direct exchange of radicles (equation 8) would be quite inapplicable to the rearrangements of azides. Triphenylmethyl halogen amines and hydroxylamines having been found, in this laboratory, to undergo normal rearrangements, the problem of the rearrangement of triphenylmethylazides $(\text{C}_6\text{H}_5)_3\text{C}.\text{N}(\text{N}_2)$ was undertaken by us. It was intended to settle three main questions. The first two were: (1) Whether a rearrangement could be effected at all; (2) Whether heat alone would not be sufficient to effect the rearrangement, this being the agent indicated by the univalent nitrogen theory of the rearrangement:



Both of these questions were easily answered in the affirmative. When the azide is heated to a high temperature, it is decomposed, with a loss of nitrogen. The course of the rearrangement was followed by the hydrolysis of the product and identification of the substances thus formed, namely aniline and benzophenone. These are the compounds which phenylimido benzophenone $(\text{C}_6\text{H}_5)_2\text{C}:\text{NC}_6\text{H}_5$ (equation 9) should

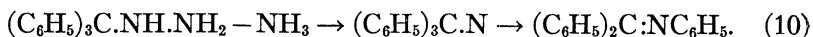
form (equation 4). The aniline obtained gave the characteristic bleaching-powder test and formed a chloroplatinate which was analyzed (33.35, 32.32% platinum found, theory 32.78%); the benzophenone was identified by its melting-point 47.5° , which was unchanged when the product was mixed with some known, pure benzophenone.

(3) The third question raised in this investigation concerned itself with the following relations: in the rearrangement of a substitution product of triphenylmethyl azide, such as $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.N}(\text{N}_2)$, a certain part of the substance would form an aniline derivative $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C.NC}_6\text{H}_5$, another part would yield a derivative of chloroaniline $(\text{C}_6\text{H}_5)_2\text{C.NC}_6\text{H}_4\text{Cl}$ (see above). The ratio may be easily ascertained by hydrolysis of the product and titration of the anilines with bromine. Now, the same situation exists in regard to the rearrangement of the corresponding hydroxylamine $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NHOH}$ and the chloroamine $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NHCl}$. If in each instance the path to the rearrangement lies through an intermediate univalent nitrogen derivative, we should have the identical product $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.N}$ in each of these cases, the azide losing nitrogen, the hydroxylamine water and the chloroamine halogen acid. The environment of the univalent-nitrogen derivative would be different in the three cases on account of differences in the physical state, the temperature, etc. But since the rearrangement is an intramolecular one, it might be little affected by environment, once the compound $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.N}$ is formed. A comparison of the ratios of aniline to chloroaniline formed in the different series could then shed some light on the question of the probability of the formation of the hypothetical intermediate univalent nitrogen derivative. On account of the difficulty of securing experimental material only a beginning has been made on this phase of the problem of these rearrangements. We have already found, however, that in the rearrangement of $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.N}(\text{N}_2)$ the ratio of aniline to chloroaniline formed is 70/30 in molar terms. This compares with the ratio¹² 71/29 found for the rearrangement of $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NHOH}$. The result speaks for itself.

That hydrazine and hydroxylamine are fundamentally similar compounds²¹ is a well-established fact, shown both by their reactions and also especially by their forming parallel derivatives, of similar properties, with a great many organic substances. One strange difference in the chemistry of these derivatives, as thus far developed, seems to have been overlooked, and that is that molecular rearrangements of hydrazines, corresponding to the rearrangements of hydroxamic acids, ketoximes, triphenylmethylhydroxylamines, etc., have not been observed, or,

apparently, even attempted; for the 'benzidine' and related rearrangements of hydrazines are of a different type. This seemed the more strange since derivatives of the third member²¹ of the group, hydrogen peroxide, have been found to undergo the same typical rearrangement²² (see part I, equation 5) as the hydroxylamine derivatives.

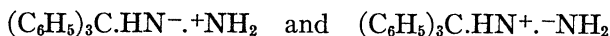
When we undertook to bridge this gap in the chemistry of the hydrazine derivatives, no difficulty was anticipated in securing such rearrangements. Not only the fundamental analogy between the groups of compounds indicated this, but, from the point of view of the univalent nitrogen theory of the rearrangements, it seemed as if there should be no difficulty in removing ammonia from triphenylmethylhydrazine and thus starting a rearrangement:



We were very much surprised to find that all our attempts to cause a rearrangement of this hydrazine and of a great many others by means of acids or zinc chloride (reagents to combine with ammonia) were complete failures. Although the experiments are being continued in spite of the original failures, these were sufficiently numerous and impressive to lead us to reconsider in greater detail the theoretical relations involved. Now, for rearranging chloroamines (*e.g.*, $(\text{C}_6\text{H}_5)_3\text{C.HN}^- + \text{Cl}$), hydroxy-

lamines (*e.g.*, $(\text{C}_6\text{H}_5)_3\text{C.HN}^- + \text{OH}$) or peroxides (*e.g.*, $(\text{CH}_3)_2\text{C} \begin{smallmatrix} \nearrow \text{O}^- \\ | \\ \searrow \text{O}^+ \end{smallmatrix}$),

the distribution of the charges on the atoms in the unstable parts of the molecules can be determined with a great degree of reliability.¹² For a hydrazide, this is not the case, no criteria having as yet been established by means of which we can distinguish, for instance, between the electromeric structures:



Obviously, however, the question of the molecular rearrangement of triphenylmethyl hydrazine could very well, and probably would, depend altogether on its electronic structure. For instance, a decomposition $(\text{C}_6\text{H}_5)_3\text{C.HN.NH}_2 \rightarrow (\text{C}_6\text{H}_5)_3\text{C.NH}_2 + (\text{HN})$ would not lead to a rearrangement and the electronic structure of the hydrazide might insure this decomposition in place of the one expressed in equation 10.

These considerations made it appear desirable to attempt the rearrangement of a symmetrical molecule, di-triphenylmethylhydrazine, about whose electronic structure there could be no doubt: $(\text{C}_6\text{H}_5)_3\text{C.HN}^+. - \text{NH.C}(\text{C}_6\text{H}_5)_3$. A loss of triphenylmethylamine from either side would leave a univalent nitrogen derivative $(\text{C}_6\text{H}_5)_3\text{C.N}$ and rear-

rearrangement should inevitably follow. Whether this argument should ultimately be found to be altogether right or not, it is a noteworthy fact that it led us to the first realization of the rearrangement of a hydrazine derivative along these lines. From the product of the action of zinc chloride on the symmetrical hydrazine, aniline was obtained and identified (by a positive chloride of lime test; by analysis of its chloroplatinate, which gave 32.80% platinum, theory 32.78%). The question as to the mechanism of the rearrangement awaits the identification of the further products of the reaction, but aniline could be formed only by a migration of a phenyl group from carbon to nitrogen, the type of rearrangement we desired to produce. This is, we believe, the first rearrangement of a hydrazine along the lines so characteristic for the hydroxylamine derivatives, which have been known for forty years. It is significant that the way to its accomplishment was pointed by the application of Thomson's original theory of electron valences to the subject of these rearrangements.

¹ J. J. Thomson, *Electricity and Matter*, 1905, and *Corpuscular Theory of Matter*, 1907.

² L. W. Jones, *Amer. Chem. J.*, **50**, 440 (1913); *Ibid.*, **48**, 1 (1912).

³ J. Stieglitz and P. N. Leech, *J. Amer. Chem. Soc.*, **36**, 272 (1914) and J. Stieglitz, *Ber. d. Chem. Ges.*, **43**, 782 (1910); **46**, 2149 (1913); *Amer. Chem. J.*, **46**, 327 (1911).

⁴ See the bibliography of the theory of the rearrangements, Stieglitz and Leech, *loc. cit.*

⁵ See a preliminary report, J. Stieglitz and Isabelle Vosburgh, *Ber. D. chem. Ges.*, **46**, 2151 (1913); also the following article.

⁶ Th. Seliwanow, *Ibid.*, **25**, 3617 (1892); F. Lengfeld and J. Stieglitz, *Amer. Chem. J.*, **15**, 215, 504 (1893).

⁷ W. A. Noyes, *J. Amer. Chem. Soc.*, **23**, 450 (1901); J. Stieglitz, *Ibid.*, **23**, 796 (1901); Walden, *Zs. physik. Chem.*, **43**, 385 (1903).

⁸ J. J. Thomson, *Phil. Mag.*, **27**, 757 (1914).

⁹ A. A. Noyes, *Carnegie Inst. Publications*, **63**, 351 (1907).

¹⁰ W. C. Bray and G. E. K. Branch, *J. Amer. Chem. Soc.*, **35**, 1440 (1913).

¹¹ G. N. Lewis, *Ibid.*, **35**, 1448 (1913).

¹² J. Stieglitz and Leech, *loc. cit.*

¹³ J. Stieglitz, *J. Amer. Chem. Soc.*, **30**, 1797 (1908). See also W. A. Noyes, *loc. cit.*

¹⁴ For the theory of the intermediate formation of univalent nitrogen derivatives, see J. Stieglitz, *J. Amer. Chem. Soc.*, **18**, 751 (1896); **29**, 49 (1903), and the literature references, Stieglitz and Leech, *loc. cit.*

¹⁵ A. Werner, *Ber. D. chem. Ges.*, **25**, 33 (1892); **26**, 1562 (1893); **29**, 1153 (1896); M. Kubara, *Mem. Coll. Sci. Engin.*, Kyoto, **6**, 1 (1913).

¹⁶ J. Stieglitz and G. Curme, *Ber. D. chem. Ges.*, **46**, 911 (1913).

¹⁷ J. Thiele, *Ibid.*, **44**, 2522 (1911).

¹⁸ J. J. Thomson, *Phil. Mag.*, **27**, 784 (1914).

¹⁹ J. Stieglitz and P. P. Peterson, *Ber. D. chem. Ges.*, **43**, 782 (1910), and P. P. Peterson, *Amer. Chem. J.*, **46**, 325 (1911).

²⁰ E. Beckmann, *Ber. D. chem. Ges.*, **19**, 988 (1886); **27**, 300 (1894).

²¹ A. Angeli, *Chem. Zentralbl.*, 1910, II, 861.

²² A. v. Baeyer, *Ber. D. chem. Ges.*, **32**, 3627 (1899).